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Tuning the Temperature Dependence for Switching in Dithienylethene Photochromic Switches

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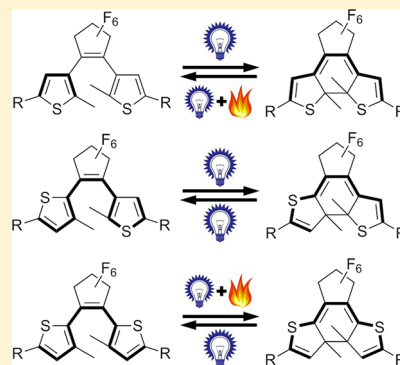
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S Supporting Information

ABSTRACT: Diarylethene photochromic switches use light to drive structural changes through reversible electrocyclization reactions. High efficiency in dynamic photoswitching is a prerequisite for applications, as is thermal stability and the selective addressability of both isomers ring-opened and -closed diarylethenes. These properties can be optimized readily through rational variation in molecular structure. The efficiency with regard to switching as a function of structural variation is much less understood, with the exception of geometric requirements placed on the reacting atoms. Ultimately, increasing the quantum efficiency of photochemical switching in diarylethenes requires a detailed understanding of the excited-state potential energy surface(s) and the mechanisms involved in switching. Through studies of the temperature dependence, photoswitching and theoretical studies demonstrate the occurrence or absence of thermal activation barriers in three constitutional isomers that bear distinct π -conjugated systems. We found that a decrease in the thermal barriers correlates with an increase in switching efficiency. The origin of the barriers is assigned to the decrease in π -conjugation that is concomitant with the progress of the photoreaction. Furthermore, we show that balanced molecular design can minimize the change in the extent of π -conjugation during switching and lead to optimal bidirectional switching efficiencies. Our findings hold implications for future structural design of diarylethene photochromic switches.



1. INTRODUCTION

Photochromic switches are a remarkable class of organic molecules that can be interconverted reversibly between two stable states with light. This property can be harnessed for optical control of structure and functionality with light. Among the photochromic switches,^{1,2} diarylethenes³ are particularly attractive compounds and have been at the focus of novel photoswitching phenomena, such as changes in fluorescence intensity and wavelength,^{4–9} magnetic properties,¹⁰ electron-transfer interactions,¹¹ conductance,^{12–16} electrochemical properties,^{17–20} and optical rotation,²¹ to cite but a few. Furthermore, the photochromic behavior of diarylethenes has been adopted to drive changes in bulk material properties and supramolecular systems, for example, modification of crystalline states,^{22–24} gelation properties,²⁵ and liquid-crystal phase changes.^{26–28} However, application of diarylethenes demands high switching efficiency over a wide range of external conditions. The efficiency of the photoreaction is related to the quantum yield of the two photochemical processes and the absorption spectrum of the chromophores. Another challenge is to realize switching over a wide range of temperatures.²⁹ Ultimately, the desired switching efficiency can be achieved predictably only by unravelling the fundamental principles that

determine the efficiency of the switching processes in these systems. To date, the majority of studies of switching efficiency have centered on theoretical investigations³⁰ and comparison of quantum yields of existing derivatives³¹ and on geometrical optimizations of reacting atoms toward ring closing.

The most common switch structure among diarylethene derivatives consists of a cyclic 1,2-ethenedienyl bridge connecting two thiophene rings at the 3-positions (referred to from here on in as *normal* switches; Figure 1a). Additional functionalization of this core with aromatic groups shifts the absorption band of the closed form toward the red, which is essential for the majority of applications.^{1,3} The closed form of these normal switches possesses a system of π -electrons delocalized over the whole molecular scaffold manifested in a continuous alternation of single and double bonds. This linear conjugation is disrupted as the closed form is switched to the open form. The photochemical quantum yields for switching from the closed to the open form (ring opening) are usually low, typically ranging from 0.001 to 0.1.³ Quantum yields for

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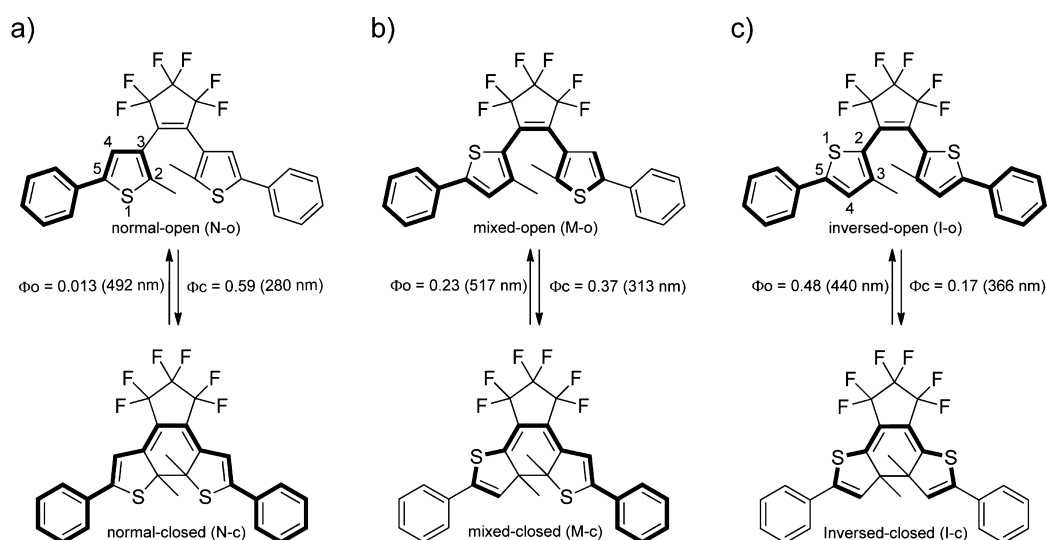


Figure 1. Structure of the switches, phototransformation, and their quantum yields for a (a) normal switch (N), (b) mixed switch (M), and (c) inversed switch (I). The thick lines highlight the longest possible delocalization of π -electrons within the structure, simplistically viewed as a system of alternating single and double bonds. The lone pair electrons on the sulfur atoms are considered to play a role in the delocalization only when there is no other possibility to extend the conjugation pathway.

the reverse process (ring closing) are, on the other hand, high, ranging between 0.2 and 0.5.³ In addition to such large differences in quantum yields, we have previously shown that whereas the ring-closing process shows negligible dependence on temperature, photochemical ring opening is strongly temperature-dependent, and below ~ 130 K, the photochemistry is effectively suppressed.²⁹

Here, we explore temperature dependence of switching of three constitutional isomers of diarylethenes with alternating extents of π -conjugation along the reaction path. Temperature-dependent studies are ideally suited to reveal the presence of thermal barriers in photochemical reactions. We demonstrate that the presence or absence of the thermal barrier correlates with the changes in the degree of π -conjugation and quantum yields. Furthermore, we demonstrate that the molecular design can be used to avoid the occurrence of thermal barriers, increasing the overall efficiency for switching.

2. RESULTS AND DISCUSSION

2.1. Structural Aspects and Photochemical Quantum Yields. Figure 1 shows three constitutional isomers of a diarylethene derivative. The essential difference between these isomers is the substitution of thiophene rings at positions 2 and 3 by the bridging hexafluorocyclopentene ring and the methyl groups. The alternating substitution permits control of the extent of delocalization of the π -electrons. π -Electrons in the normal open switch (N-o) (Figure 1a) are symmetrically localized on each of the thiophene units of the molecule. In the closed form, the system of single and double bonds in N is rearranged, and the π -electrons are delocalized over the whole molecule. In contrast, for the inverse switch (I) (Figure 1c), a fully delocalized system of π -electrons is present in the open form, the extent of which decreases when the molecule is switched to the closed form. An asymmetric mixed switch M that bears a delocalized π -system intermediate between those of N and I was prepared also (Figure 1b). The extent of delocalization is similar in the open (M-o) and closed (M-c) forms. We expected that the switching efficiency of M will be intermediate between that of N³² and I.³³ All three switches

exhibit fully reversible switching behavior when irradiated with light of appropriate wavelength. The quantum yields for ring opening of N-c ($\phi = 0.013$) and ring closing of I-o ($\phi = 0.17$) are low (Figure 1). The reverse processes in N and I on the other hand show relatively high efficiency (N-o to N-c: $\phi = 0.59$; I-c to I-o: $\phi = 0.48$) (Figure 1). In contrast, quantum yields for ring opening and ring closing in M are both relatively high (Figure 1b). Bidirectional switching can therefore be considered to be efficient in M. It should be noted that the efficiency of ring closing and ring opening in M is reduced when compared to ring closing in N and ring opening in I, respectively. This can be rationalized by considering that M does not possess the difference in conjugation between the closed and open forms that drives closing of N and opening of I, respectively, toward greater extent of conjugation.

2.2. Electronic Properties As a Function of Structure.

The UV/vis absorption spectra of all three compounds are shown in Figure 2a–c. The increased delocalization of the π -electrons over the switching unit is manifested in a bathochromic shift. For the open forms of the switches, the lowest-energy absorption band shifts undergo a bathochromic shift from N to M and finally to I. For the closed forms, the trend is reversed, and the shift is bathochromic from I to M and N. Identical shifts in λ_{max} values of N, M, and I were calculated at the TDDFT level (Table 1). M can be intuitively described as a compound with intermediate electronic properties although some caution should be exercised as M is nonsymmetric and more electronic transitions need to be considered. The observed behavior can be rationalized, to a first approximation, based on the extent of delocalization of the π -electron systems. The rigidity of the molecules plays a role also, as demonstrated by the spectrum of I (Figure 2c). The lowest-energy absorption band of the open form of I is shifted to shorter wavelengths compare to the closed form. The extent of delocalization of π -electrons is less in the open form due to the conformational freedom of I-o, and hence, the π -electrons are thus inefficiently delocalized. The same effect is observed for M, where both forms have similar extents of conjugation but differ in rigidity. The longest-wavelength absorption band of M-c is in the visible

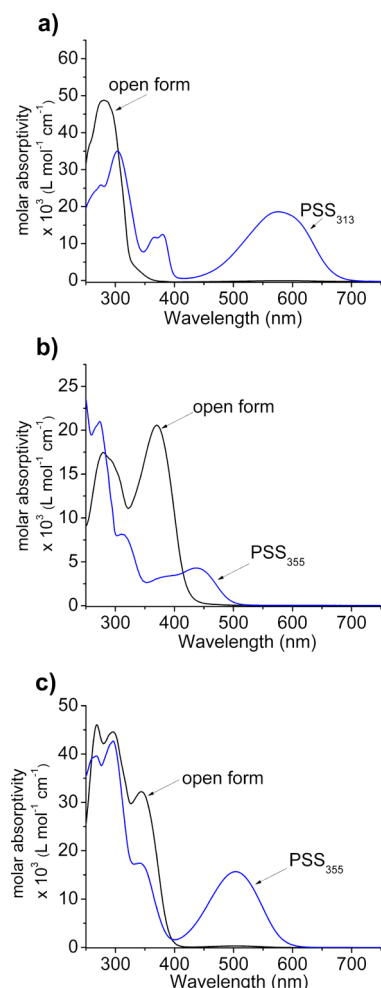


Figure 2. UV/vis absorption spectra of the dithienylethene switches in the open forms (solid line) and PSSs (dashed line) upon irradiation at $\lambda = 313$ (normal switch) or 355 nm: (a) normal switch (N), (b) mixed switch (M), (c) inversed switch (I).

Table 1. Calculated^a and Experimental λ_{max} (nm)

type	closed		open	
	λ_{max} (calc.) (nm)	λ_{max} (expt.) (nm)	λ_{max} (calc.) (nm)	λ_{max} (expt.) (nm)
normal	602	575	296	280
mixed	521	503	379	344
inverse	455	438	406	370

^aCalculated λ_{max} were obtained from HOMO \rightarrow LUMO vertical excitation energies at the TDDFT(B3LYP)/6-31G* level.

region, while the lowest wavelength absorption band of **M-o** is in the UV region. This has implications for the addressability of **M**; both forms can be effectively addressed using light of different wavelengths. The relative absorbance of each form at a certain wavelength together with the corresponding quantum yields determines the photostationary states (PSSs) of the switches upon irradiation.³⁴ This can be considered as a measure of switching efficiency also. At the PSS at 355 nm, **M** in hexane (Figure 2b) contains 83% closed form (Supporting Information). At the PSS at 355 nm, **I** contains 91% closed form, while switch **N** contains 97% of the closed form.³²

2.3. Thermal Activation of Switching and Arrhenius Parameters. The temperature dependence of the photo-

chemical switching was investigated over the temperature range of 115–290 K (Figure 3a–f). The data points were plotted for the wavelength corresponding to the maximum absorption of the closed forms. The molar absorptivity at the maximum absorption increases with decreasing temperature as the bands get sharper. This has an effect on the overall shape of the kinetic curves (Figure 3a–f); however, it does not influence the rate constant determination. The corresponding rate constants were obtained by fitting the data as a monoexponential process. This method used was validated for determination of rate constants of diarylethenes earlier.²⁹

Arrhenius plots are shown in Figure 4. The rates of photochemical reactions are dependent on the incident light intensity; however, the exponent of the fit from Arrhenius plots is intensity-independent, and the activation energy necessary for the thermally activated reaction to occur can be calculated from these plots.²⁹ Ring closing of **N** does not show a dependence on temperature within the temperature range studied (Figure 4a), whereas ring opening was found to be temperature-dependent (Figure 4b). From fitting of the rates for ring opening, the activation energy (E_a) was determined as $9.3 \pm 0.3 \text{ kJ} \cdot \text{mol}^{-1}$ with the cutoff temperature below 130 K, below which ring opening does not occur. The inversed switch **I** shows an opposite dependence on temperature. Ring closing of **I** is temperature-dependent ($E_a = 9.8 \pm 2.0 \text{ kJ} \cdot \text{mol}^{-1}$), and below 170 K, ring closing is not observed, while ring opening is not temperature-dependent (Figure 4b). The mixed switch **M** exhibits markedly different behavior (Figure 4). Ring closing is essentially temperature-independent, and the ring opening shows only a slight temperature dependence, with $E_a = 2.3 \pm 0.2 \text{ kJ} \cdot \text{mol}^{-1}$, and hence, switching occurs readily over the temperature range examined. The experimentally found temperature dependence of the switching rates **N**, **I**, and **M** are consistent with our hypothesis that the occurrence of the thermal barrier is related to the decrease in the extent of delocalization of π -electrons. In the case of **M-o**, the decrease in the extent of delocalization is ascribed to the decreased molecular rigidity rather than the number of π -electrons available for conjugation.

2.4. Origin of the Barriers to Ring Opening and Closing in N, I, and M. The photochromism (ring opening and closing) of diarylethenes belongs to the class of photochemical 6π -electrocyclic reactions that proceed in a conrotatory fashion.^{35,36} A detailed theoretical study of the configuration correlation diagrams and potential energy surface for **N**^{37–39} and **I**^{30,40–42} has elucidated the mechanism and orbital symmetry bases for the switching (Figure 5). The ground state 1A is accompanied by a bright singlet excited state 1B (arising from a HOMO \rightarrow LUMO single excitation) and a dark singlet excited state 2A (arising from HOMO–1 \rightarrow LUMO and HOMO \rightarrow LUMO+1 single excitations and a HOMO \rightarrow LUMO double excitation predominantly in the “pericyclic minimum” (PMIN) region), denoted by C_2 irreducible representations. These states participate in the photochemical electrocyclic reactions.⁴³ The pathway followed in the photochemical electrocyclic reaction is generally expressed using a “modified” van der Lugt-Oosterhoff (L-O) model (Figure 5).^{44,45}

Of special interest in the present study is the origin of energy barriers and hence the temperature dependence in the photochemical ring-opening and ring-closing reactions.

The modified L-O reaction pathway presents two pathways to include a barrier (see Figure 5):

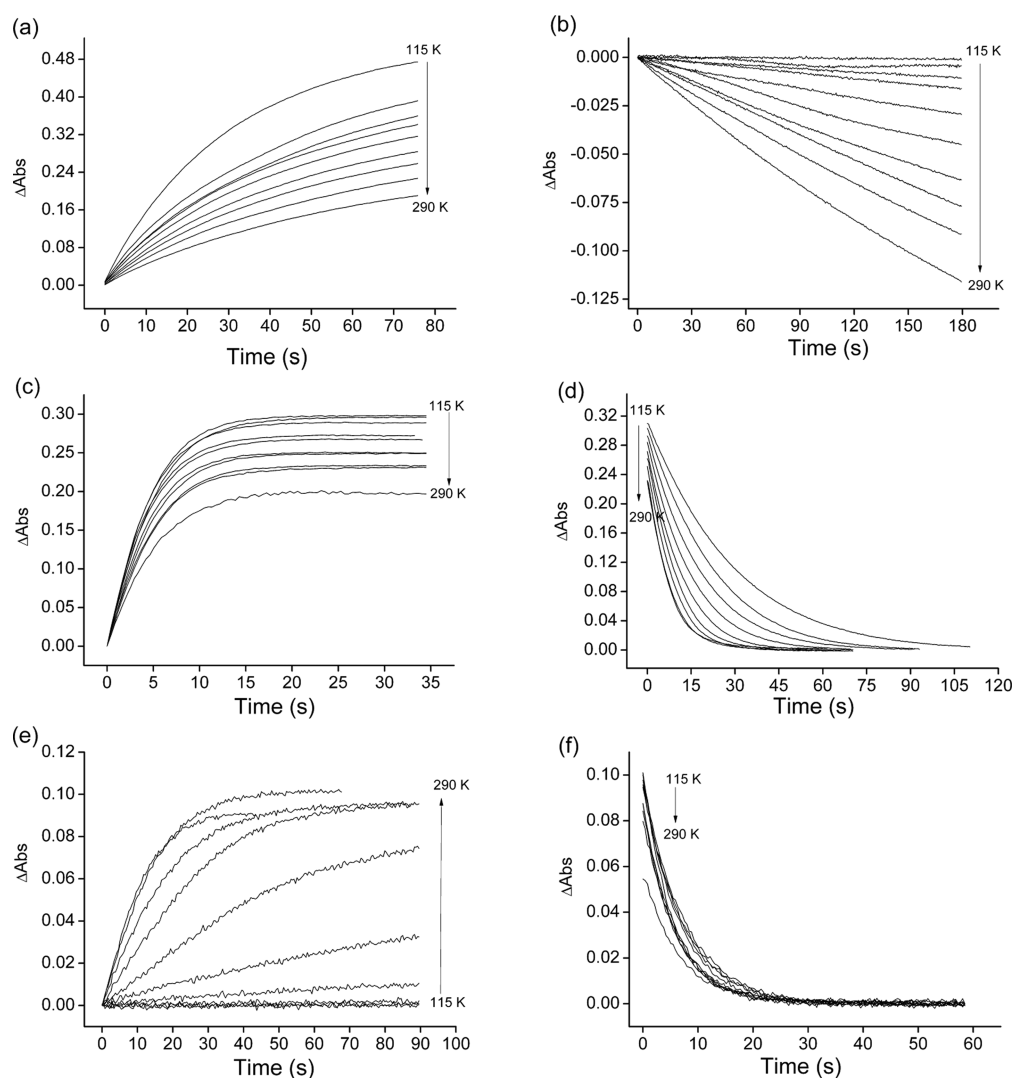


Figure 3. Temperature-dependent kinetics of (a) ring closing for **N**, (b) ring opening for **N** (the absorbance at 575 nm at all temperatures was normalized to 0.25, which corresponded to absorbance at 290 K), (c) ring closing for **M**, (d) ring opening for **M**, (e) ring closing for **I**, and (f) ring opening for **I**.

(1) Nonradiative decay from 1B to 2A, that is, from 1B_{CMIN} (1B minimum point in the closed form region) to 2A_{PMIN} through (a vicinity of) 1B/2A CI_C (1B/2A CI in the closed form region) for opening and from 1B_{OMIN} (1B minimum point in the open form region) to 2A_{PMIN} through (a vicinity of) 1B/2A CI_O (1B/2A CI in the open form region) for closing.

(2) Nonradiative decay from 2A to 1A, that is, from 2A_{PMIN} to 1A through S₁/S₀ CI for both ring opening and closing (although the PMIN structure could most probably be deformed largely from C₂ symmetry;⁴⁶ we conveniently use the C₂ irreducible representation to refer to this point as 2A_{PMIN}).

These two scenarios are based, in the case of both ring opening and ring closing, on passing through the common PMIN region, as shown in the modified L-O model. The observed differences in the temperature dependences of the ring-opening/closing reaction rates is expected to be due to the 1B → 2A decay pathway (vide infra) and not the energy barrier to the 2A → 1A decay pathway that is common for opening/closing. State correlation diagrams of **N**, **M**, and **I** along the conrotatory (C₂ symmetry) paths, depicted in Figure 6, are based on the B3LYP/TDB3LYP levels^{47,48} of 1A, 1B Franck–

Condon (1B_{FC}), and 2A_{FC} energy levels of the closed and open forms, where the minimum energy of the 1A state of the open form of **N** is set at zero. These calculated energy levels reflect the extent of conjugation of the closed and open forms of **N**, **M**, and **I**. Considering the reaction pathway in the L-O model (Figures 5 and 6), for **N**, there is a barrier through the 1B/2A CI_C for opening but no such barrier to closing, for **M**, there is a smaller barrier to opening and again no barrier to closing, and for **I**, there is no barrier to opening and a barrier through 1B/2A CI_O to closing. The energy barrier predicted by the state correlation diagrams for **N**, **M**, and **I** are in full agreement with the empirical data (Figure 4). Therefore, the temperature dependence of photochemical ring-opening/closing reactions in these diarylethenes can be considered to be caused by the energy barriers of the 1B → 2A decays.

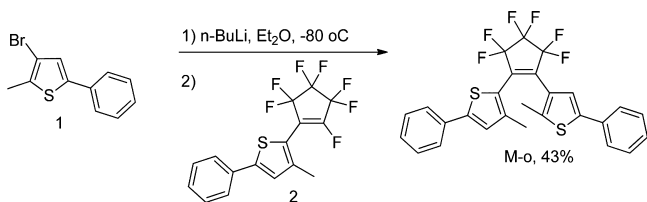
Furthermore, it should be noted that the temperature dependence of photochemical ring-opening and -closing reaction rates, that is, activation energies for decay by the 1B → 2A route, correlate with the quantum yields for photochromic ring-opening/closing reactions. The photochemical ring-opening/closing reactions that do not show a thermal activation from the 1B_{FC} state toward the 2A_{PMIN}, that is,

switching. In order to design efficient switches in terms of bidirectional switching, the change in overall delocalization in reactants and products should be kept to a minimum. This can be achieved by keeping the length of π -conjugated system the same in combination with increased rigidity in the molecule. The limitation of this approach, however, is the reduced photoconversions for switches with similar absorptivity of the open and closed forms at the irradiation wavelength. Designing switches with distinctively different absorptivity at required wavelengths while keeping the delocalization changes to a minimum should help to surpass this limitation.

We have shown a correlation of the quantum yields of the photoswitching with physical phenomena that can be tested and understood experimentally. This correlation is potentially more generally applicable to various classes of photochromic switches, and hence, the present data will contribute to the design of efficient photoswitches and their successful incorporation in various applications and into switchable molecular-based devices.

4. METHODS

For all spectroscopic measurements, UVASOL-grade solvents (Merck) were employed. All reagents employed in the synthetic procedures were of reagent grade or better and used as received, unless otherwise stated. Mass spectra (HRMS) were recorded on an AEI MS 902. Melting points were recorded on a Büchi B-545 melting point apparatus. ^1H and ^{13}C NMR spectra were recorded on a Varian AMX-400 (400 and 100.59 MHz) in CDCl_3 . Chemical shifts are reported in ppm with the residual solvent signal as the internal standard (CHCl_3 : δ 7.26 for ^1H and δ 77.0 for ^{13}C). Compounds **N** and **I** were prepared according to procedures reported earlier.^{32,33} **M** was prepared following a synthetic strategy generally employed to synthesize perfluorocyclopentene-diarylethenes according to the scheme below from **1** and **2**, the latter being a side product from the synthesis of **I**.



4.1. Synthesis of M-o. A solution of **1** (290 mg, 1.16 mmol) in dry diethyl ether (10 mL) was cooled to $-80\text{ }^\circ\text{C}$ under a nitrogen atmosphere. *n*-Butyl lithium (0.8 mL, 1.6 M solution in hexane, 1.27 mmol) was added, and after 2 h, **2** (212 mg, 0.58 mmol) dissolved in 1 mL of ether was added. The reaction mixture was stirred for a further 2 h at $-80\text{ }^\circ\text{C}$ after which the reaction was allowed to warm to ambient temperature. After an additional 2 h, the reaction mixture was diluted with diethyl ether (50 mL), washed with dilute hydrochloric acid (1%, 30 mL), saturated aqueous sodium bicarbonate (50 mL), and water (50 mL), and extracted with diethyl ether ($2 \times 25\text{ mL}$). The combined ether phases were dried over anhydrous Na_2SO_4 and filtered, and the solvent was evaporated in vacuum. Purification was by column chromatography (hexane on silica), yielding **M-o** as a solid (130 mg, 43%). ^1H NMR (400 MHz, CDCl_3): δ 1.81 (s, 3H), 2.03 (s, 3H), 7.06 (s, 1H), 7.31 (s, 1H), 7.33 (t, $J = 6.9\text{ Hz}$, 2H), 7.4 (m, 4H), 7.58 (m, 4H) ppm. ^{13}C NMR (100.59 MHz, CDCl_3): δ 14.5 (q), 15.6 (q), 122.4 (s), 122.6 (d), 125.6 (d), 125.8 (d),

126.0 (s), 126.6 (d), 127.9 (d), 128.5 (d), 129.0 (d), 129.0 (d), 133.1 (s), 133.3 (s), 141.6 (s), 142.0 (s), 142.2 (s), 147.7 (s) ppm. HRMS (APSI): calcd. for $\text{C}_{27}\text{H}_{18}\text{F}_6\text{S}_2$ 521.083, found 521.084. mp $130.6\text{--}131.7\text{ }^\circ\text{C}$.

UV/vis absorption spectra at room temperature were recorded on a JASCO V-630 spectrophotometer. The PSS of **M** was determined by HPLC. The PSS of **I** was from the known molar absorptivity ratio (4.34) of the open form at 370 nm in hexane (22800) and the closed form at 438 nm (5250).¹⁶ The PSS of the switch **N** obtained by irradiation of light with a 313 nm wavelength contained 97% of the closed form and was reported previously.¹⁵ Temperature-dependent measurements were performed between 115 and 290 K using a liquid-nitrogen-cooled optical cryostat (Optistat-DN, Oxford instruments). Isopentane solutions of all three compounds, with concentrations of 1.92×10^{-5} (**N**), 2.34×10^{-5} (**I**), and $1.96 \times 10^{-5}\text{ mol}\cdot\text{dm}^{-3}$ (**M**) were used. A Nd:YAG pulsed laser (Spitlight 400, Innolas) at 355 nm (10 Hz, 3 mJ per pulse) was used to ring-close the samples. A 473 nm continuous laser (DPSS Cobolt Blues, 50 mW, cobolt) was used to drive ring opening. In order to minimize artifacts due to diffusion, the entire sample volume (1 cm^3) was irradiated by expanding the beam. The photoconversion was monitored in time by the absorbance at the maximum in the visible region. The data points were plotted for the wavelength corresponding to the maximum absorption of the closed forms. Kinetics at various temperatures were recorded by fiber optic UV/vis spectrometer (AvaLight-DH-S deuterium-halogen fiber coupled light source, 215–2500 nm, controlled by AvaSpec-USB2 software via an IC-DB26-2 interface cable coupled with an Avaspec 3648, UA, slit 25, 200–1100 nm CCD detector with a deep-UV coating, Avantes) with the halogen lamp switched on and the deuterium lamp switched off (only the visible part of the spectrum can be recorded in this arrangement) and equipped with a long-pass filter at 420 nm. In principle, the light from the spectrometer light source can cause photochemistry. However, with the aforementioned setup, repetitive acquisitions showed no detectable changes in the absorption spectra.

Quantum yields for ring closing and ring opening of **M** were determined in hexane at room temperature. Light of appropriate wavelengths (313 nm for ring-closing and 517 nm for ring-opening reactions) was isolated by passing the output of the medium pressure mercury and Xe lamps through a monochromator (Jobin Yvon UV-10) with a long-pass filter (Toshiba Y-43, 430 nm) and compared with bis-1,2-(2-methylbenzothiophen-3-yl)perfluorocyclopentene as a standard.¹⁴ For the cyclization reaction, the initial slopes of the enhancement of photogenerated closed-ring isomers were compared to that of the standard, and for the cycloreversion reaction, the initial decrease of the closed-ring isomer upon visible light was compared with the eq 1, where the $A(t)$ and $A(0)$ are the time-dependent and initial absorptions and ϵ , ϕ , and I are the absorption coefficient, quantum yield, and light intensity, respectively, according to the literature.⁴⁹

$$\log A(t) = \log A(0) - \epsilon\phi It \quad (1)$$

4.2. Calculations. The ground-state (S_0) optimized structures were obtained at the hybrid density functional theory (DFT) (with the B3LYP xc functional) level. The vertical excitation energies (absorption maximum wavelengths) were calculated using the time-dependent density functional theory (TDDFT) with the B3LYP functional at the B3LYP S_0 optimized structures. We employed the 6-31G* basis set in all

of the calculations. All computations were performed with Gaussian03.^{47,48,50} The accuracy of the current method is demonstrated by comparison of calculated and empirical values of λ_{max} of absorbance for N, M, and I in Table 1 and Figure 5. The calculated λ_{max} were obtained from HOMO \rightarrow LUMO vertical excitation energies at the TDDFT(B3LYP)/6-31G* level. As shown in Figure 5, the calculated TDDFT(B3LYP) λ_{max} reproduce the differences between the experimental λ_{max} of the closed and open forms of N, M, and I. Therefore, the HOMO \rightarrow LUMO Franck–Condon (FC) states of these three types of diaryl ethenes calculated at the TDDFT(B3LYP) level are considered to be reliable.

■ ASSOCIATED CONTENT

■ Supporting Information

Details and coordinates of density functional calculations, HPLC, and temperature dependence plots. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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